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(54) Title: **UPGRADING ILMENITE FOR TITANIA PRODUCTION**

(57) Abstract: The present invention provides a process for upgrading a primary ilmenite containing gangue mineral grains for forming titania pigment by the sulfate method, the process including the step of: roasting a primary ilmenite containing gangue mineral grains at a temperature of less than 650°C under conditions that promote the formation of a magnetically separable product rich in titania and in which the rutile present is in a form that is at least partially soluble in concentrated sulfuric acid. The process will typically involve the step of: subjecting the roasted ilmenite concentrate containing gangue to magnetic separation to reduce the content of gangue mineral grains and provide a product rich in ilmenite and containing rutile.

UPGRADING ILMENITE FOR TITANIA PRODUCTION

The present invention relates to a process for upgrading a primary ilmenite concentrate for production of titania pigment by the sulfate method.

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The mineral ilmenite, ideally FeTiO_3 , is important economically as the major feedstock used for titania pigment production. Ilmenite has an ideal composition of 52.7% TiO_2 , but naturally occurring ilmenites may have TiO_2 contents ranging from 40-60%. Ilmenite may contain hematite (an iron oxide) in solid solution resulting in it having less than the ideal amount of TiO_2 . Weathering of the ilmenite results in oxidation and leaching of iron out of the mineral so it contains a higher TiO_2 content than the ideal amount. Here a primary ilmenite may be considered to have a TiO_2 content of up to 58% depending on the provenance of the ilmenite.

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Ilmenite is used either directly, or after upgrading to a high-titania synthetic rutile (SR) or titania slag. There are two major methods for converting ilmenite or its upgraded products to titania pigment. The sulfate method involves digestion of ilmenite or slag in concentrated sulfuric acid, followed by separation of iron sulfate and crystallisation of pure titania. The chloride method involves high temperature chlorination of ilmenite, SR or slag to form TiCl_4 which is then oxidised to form rutile and regenerate chlorine. The two methods each account for approximately 50% of titania pigment production.

25 Requirements for a suitable feedstock for the sulfate method include a high ferrous iron content to provide a high exothermic heat of sulfation to maintain the autogenous digestion reaction, a low level of rutile contaminant in the ilmenite. Rutile presents a problem because it is generally insoluble in sulfuric acid. It is also preferable to have low levels of elements that could impart a colour to the pigment. Chromium is a particular problem in this latter regard and pigment feedstock specifications require chromium contents lower than 0.2 wt% Cr_2O_3 , and preferably at around 0.1 wt% Cr_2O_3 for the sulfate process. Chrome spinels, of which the mineral chromite is an example, are the main sources of chromium in ilmenite concentrates.

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In Australia the main ilmenite supplies to the sulfate process come from alluvial sand deposits along continental coastlines. Australia has been a major provider of such feedstocks, which are mainly from Western Australian coastal deposits.

5 These ilmenite concentrates are very low in chrome spinel contaminant grains. As the high quality deposits are being progressively exhausted, attention is being directed to new deposits such as the vast resources of heavy mineral sands in the Murray Basin in south eastern Australia, and the East coast South African deposits. Ilmenite concentrates produced from these deposits are

10 usually contaminated with chrome spinel grains, which cannot be easily removed from the ilmenite by conventional physical separation methods.

A number of prior art processes have demonstrated that ilmenite grains can be effectively separated from grains of various other gangue minerals, including

15 chrome spinels, by using a magnetising roast followed by magnetic separation. The roast selectively enhances the magnetic properties of the ilmenite grains. For example, an oxidation roast at $\sim 800^{\circ}\text{C}$ is used commercially by Richards Bay Minerals (South Africa) to lower the chrome spinel content of their primary ilmenite concentrate from 0.3 to 0.1 wt% of Cr_2O_3 , prior to smelting the ilmenite

20 to form a high titania slag. The magnetising roast used by Richards Bay Minerals is described by Lee and Poggi (1978). Shelly (1993) describes a reduction roast using metallurgical coke at 800°C to enhance the magnetism of ilmenite grains and allow them to be magnetically separated from tantalum minerals in order to obtain a low grade tantalite concentrate. Walpole (1992)

25 has patented a process for separation of ilmenite from mineral mixtures using a fluidised bed magnetising roast in the presence of excess carbon to provide a controlled oxygen atmosphere, followed by magnetic separation of the magnetised ilmenite. The preferred roasting temperature range was given as 750 to 850°C .

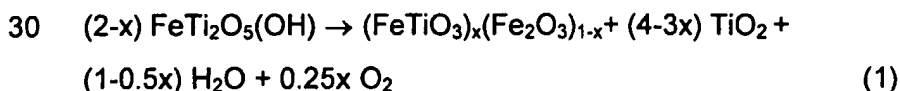
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It is generally accepted (Nell, 1999) that a magnetising roast works due to the formation of a ferrimagnetic solid solution between ilmenite and hematite, $(\text{FeTiO}_3)_x(\text{Fe}_2\text{O}_3)_{1-x}$. The magnetic susceptibilities of such solid solution phases are several times higher than that of ilmenite for solid solution compositions.

containing between about 10 and 60 mole% of the hematite component (Nell and den Hoed 1997). Nell (1999) has explained how suitable magnetic properties can be achieved for both primary ilmenites (containing predominantly Fe^{2+}) and highly weathered ilmenites (iron mainly as Fe^{3+}) by adjusting the gas atmosphere in the magnetising roast. Merritt and Cranswick (1994) reported that the enhanced magnetism obtained by fluid bed roasting of ilmenite in the presence of excess carbon at about 800°C was at least partly due to the formation of a thin shell of magnetite on the ilmenite grains.

When a magnetising roast is used to clean an ilmenite concentrate for use as a sulfate-route pigment feedstock, a second important criterion for the roast is that the formation of rutile is kept to a minimum. This is because crystalline rutile is insoluble in concentrated sulfuric acid and it can cause problems in the digester operation as well represent a loss of titania. The problem of rutile formation during roasting is accentuated for weathered ilmenites due to a higher titania content in the altered ilmenite grains. During weathering of ilmenite, the iron is oxidised and partially leached from the grains to form a hydrated ferric titanate mineral called pseudorutile. Pseudorutile is stable over a range of compositions. A simple representation of its mean composition has been given by Ignatiev (1999) as $\text{FeTi}_2\text{O}_5(\text{OH})$. Further weathering eventually results in the formation of leucoxene, containing mainly rutile.

Commercial primary and secondary ilmenite concentrates derived from mineral sands deposits commonly contain pseudorutile as the major phase. In secondary ilmenite concentrates the pseudorutile content can be as high as 80-90 wt%. When such concentrates are roasted under reducing conditions to form magnetic ferrian ilmenite, large amounts of rutile are co-formed according to reactions such as (1).



According to reaction (1), roast conditions which convert pseudorutile to a strongly magnetic ferrian ilmenite phase with $x = 0.3$, for example, produce an

approximately equal amount of rutile. This presents a significant problem in feedstock for pigment manufacture due to the insolubility of the rutile in sulfuric acid.

- 5 The present invention seeks to overcome the problem of formation of sulfuric acid insoluble rutile during the magnetising roast of altered ilmenite and provide an improved process for both removing gangue minerals such as chrome spinels and maintaining high acid solubility of the roasted product.
- 10 We have found, surprisingly, that when primary ilmenite is roasted under conditions that involve low roast temperatures and preferably short roast times, the rutile formed in reaction (1) is reactive and a major proportion of it can be dissolved in sulfuric acid under conditions that simulate the sulfate-route digestion process.
- 15 We have found that the roasting temperature is the critical parameter for the roasted product to maintain a high acid solubility. In particular, we have found that if the roast temperature is maintained below about 650°C, the rutile formed is largely soluble in simulated acid digestion conditions. At higher temperatures
- 20 the extent of solubility of the rutile decreases rapidly with increasing temperature. At roast temperatures used commonly in prior art processes (~800°C) the rutile would be well crystallised and would present problems in the sulfate method acid digestion process. We believe that the high solubility of the rutile when formed at temperatures below 650°C is due to it having a very small
- 25 crystallite size ($\leq 100 \text{ \AA}$, based on measured X-ray diffraction line broadening) and thus a high surface area. The crystallite size is controlled by solid state and grain boundary atomic diffusion. These processes have a high activation energy which means that the crystallite size will increase rapidly with increasing temperature, explaining the observed rapid loss of titania solubility when the
- 30 roast temperature is increased above about 650°C.

Accordingly, the present invention provides a process for upgrading a primary ilmenite containing gangue mineral grains for forming titania pigment by the sulfate method, the process including the step of:

roasting a primary ilmenite containing gangue mineral grains at a temperature of less than 650°C under conditions that promote the formation of a magnetically separable product rich in titania and in which rutile present is in a form that is at least partially soluble in concentrated sulfuric acid.

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The process will typically involve the step of:

subjecting the roasted ilmenite concentrate containing gangue to magnetic separation to reduce the content of gangue mineral grains and provide a product rich in ilmenite and containing rutile.

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The main process parameter controlling the solubility of rutile formed by roasting is temperature. Temperatures above 650°C promote the formation of insoluble rutile. The temperatures used in the roasting step of the invention is typically from 500°C to 650°C. Temperatures in the range 525°C to 650°C have been found to represent a good compromise between avoiding rutile crystal growth and obtaining enhanced magnetism in relatively short roast times. The temperature range of 575°C to 640°C is most preferred.

We have recently shown that certain ilmenite samples have an appropriate mixture of ferrous and ferric iron to give an enhanced magnetic roast product simply by heating at around 600°C in an inert atmosphere (Grey and Li, 2001). For such samples an appropriate controlled oxygen potential is not necessary. The only requirement is the input of heat to bring about long-range magnetic ordering of a ferrian ilmenite phase. Dehydroxylation of pseudorutile in the altered samples during the low temperature roasts is considered to be a key factor in increasing the magnetism in the samples. For short roasting times, a roasting temperature of at least 500°C is required to initiate such reactions and this corresponds to the temperature at which most of the structural water is lost from pseudorutile. It is likely that the excess heat input to the samples required to overcome the activation energy for the endothermic dehydroxylation reactions provides the driving force for the atomic diffusions involved in increasing the magnetism of the samples.

The enhanced magnetism can be achieved in the primary ilmenite concentrate

by roasting in a non-reducing gas mixture such as fully combusted natural gas, in an inert gas such as nitrogen, in a oxidising gas in the presence of oxygen or in similar gas compositions where the oxygen partial pressure can be controlled using either a mixture of oxidising and reducing gases or by using an excess of
5 a solid carbonaceous material, such as coal, char or petroleum coke, as described by Walpole (1992). The option of using a controlled partial pressure of oxygen allows the roast to be extended to more primary ilmenites, for which the atmosphere is relatively oxidising.

10 The roasting time will be a function of the reactivity of the ilmenite sample and the driving force provided by the gas atmosphere. Roasting times as short as 10-15 min have been found to give suitably enhanced magnetic properties for certain ilmenite concentrates. Other samples require roasting times of up to 12 hours.

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The appropriate roasting time will also depend on the type of reactor used in the roasting step. In a particularly preferred process a fluidised bed reactor is used and roasting is carried out for a period of from 15 minutes to 4 hours. Preferably 15 minutes to 2 hours and most preferably 15 minutes to 90 minutes.

20 Rotary kilns may be used in the roasting step but will generally require a longer roasting time than rotary kilns where conditions are otherwise the same.

Roasting may be carried out in a fluidised bed with the selected gas composition as the fluidising gas, in a static bed in an atmosphere of the
25 selected gas composition, or in a rotary kiln furnace in the appropriate gas composition.

Magnetic separations may be achieved by using any conventional or novel magnetic separators. For example with rare earth roll or drum magnetic
30 separators, by wet high intensity magnetic separators, lift type magnetic separators or rotating magnetic field separators.

The process of the invention may include the step of digesting the product rich in ilmenite in sulfuric acid to dissolve at least part of the product. At least part of

the rutile present will be dissolved.

In the sulfate process for titania pigment production ilmenite is digested in a batch operation in 85-92 wt% sulfuric acid at about 160°C to form a porous cake. The digestion cake is contacted with water or dilute sulfuric acid and the resulting liquor is separated and contacted with scrap iron to control the oxidation states of the iron and titanium. The titanium is precipitated from the solution as a hydrous titanium dioxide by hydrolysis. An example of this process is described by Loughbrough (1992).

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Blacklow (1993) has described the digestion conditions used in the Burnie plant of Tioxide Australia. The ilmenite was dry ground to a uniformly ground product and was added to concentrated sulfuric acid in the digester with mild agitation by the addition of compressed air. After mixing the exothermic reaction was initiated by the addition of a precisely measured volume of water or recovered filtrate. Air agitation was increased during the 12-16 minutes of the reaction and then it was reduced to a trickle as the mass was left for 90-120 minutes. Dissolving fluids (hot water, cold water and recovery liquors) were then contacted with the mass for 5-7 hours and then separated and treated for recovery of the dissolved titanium.

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Work in CSIRO Minerals reported by Grey, Lanyon and Stranger (1996) has led to the development of a laboratory procedure that simulates the sulfate pigment plant digestion process. As in the pigment plant, the samples are ground and screened to obtain $-45\text{ }\mu\text{m}$ material for digestion. The grinding is done in a steel rod mill with three separate stage grinds, with intermediate screenings to avoid over-grinding. The ground sample is wetted with concentrated sulfuric acid at 60°C. Dilute acid is then added to establish the required acid strength of 92% and to provide heat of mixing that sets off the digestion reaction. The slurry is stirred until the reaction mixture thickens and gels to form the digestion 'cake'. The cake is baked for 1 h at a temperature of 160-170°C. The cake is chipped out of the reactor, crushed and sieved at 2 mm and then leached for 4 h at 60°C in 80 mls of 10% H_2SO_4 with stirring. The leach solution is filtered and the residue washed twice with 20% sulfuric acid, three times with distilled water and

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then dried in an oven overnight at 110°C before ashing at 800°C. The ashed residue is weighed and analysed by XRF and the solubility values are calculated. The validity of this laboratory procedure has been confirmed by comparison of the performance of a number of ilmenites under laboratory and plant conditions. An ilmenite with a titania solubility of over 93% in this laboratory procedure has been shown to be a suitable feedstock for a sulfate-route pigment plant.

Evaluating the performance of ilmenites for the sulfate process by the digestion test is a time-consuming operation. To obtain similar indicative information, a shorter test involving a leach in 71% sulfuric acid was developed in CSIRO Minerals. In this test the ilmenite sample is micronised and added to a solution of 71% sulfuric acid which has been heated to $176 \pm 2^\circ\text{C}$. The slurry is stirred for 15 minutes and then the reaction is quenched by immersing the reaction vessel in cold water. The residue is collected, washed, dried at 110°C and weighed and the mass solubility values are calculated. Comparison of the results with the performance of samples in a commercial sulfate-route pigment plant has shown that ilmenites that give a mass solubility of 90% or higher in this test usually are a satisfactory feedstock.

Both the 71% sulfuric acid leach and the 92% sulfuric acid digestion were used to evaluate the properties of the products prepared in the roast tests. In many cases at least 50% of the rutile present in the roasted product is soluble in the sulfuric acid.

Throughout the description and claims of this specification, the word "comprise" and variations of the word such as "comprising" and "comprises", is not intended to exclude other additives or components or integers.

The invention is further described and illustrated by the following non-limiting examples.

EXAMPLE 1

Table 1 gives chemical analyses of a Murray Basin ilmenite concentrate that

contains 0.70 wt% Cr_2O_3 (equivalent to about 2 wt% of chrome spinel contaminant grains). The ilmenite was roasted for 45 min at 700°C in a 30 mm internal diameter fluidised bed reactor using a mixture of 80 wt% ilmenite plus 20 wt% of crushed char. The fluidising gas was a mixture of 50% air and 50% nitrogen. The roast product was quenched in air, then magnetically separated using a laboratory Carpco induced roll magnetic separator.

A magnetic fraction was obtained at 81 wt% recovery for which the chromia content was lowered from 0.70 wt% Cr_2O_3 to 0.08 wt% Cr_2O_3 (Table 1). A quantitative XRD phase analysis was conducted on the magnetic fraction that showed that the majority of the pseudorutile had been converted to ferrian ilmenite and rutile. The rutile crystallite size was determined from the XRD peak broadening to be 190 Å.

The solubility in 71% H_2SO_4 at 176°C was measured. Work in CSIRO Minerals has shown that this test gives a good indication of potential sulfate-route solubility. Solubilities of higher than 90% have been found to correspond to acceptable full-scale plant digestion performance. The 700°C roasted sample gave a low mass solubility of only 79.3%. The amount of the insoluble fraction corresponds closely to the amount of rutile in the roast product as shown by the results in Table 1.

This example shows that while a roast at 700°C can give a product with a low chromia content, the solubility of the product in sulfuric acid was too low to make it an acceptable feedstock for the sulfate pigment process because of the amount of coarse grained rutile that was formed.

EXAMPLE 2

A second portion of the ilmenite used in Example 1 was given a similar roast for 45 min in a 30 mm internal diameter fluidised bed reactor using a mixture of 80 wt% ilmenite plus 20 wt% of crushed char and a fluidising gas mixture of 50% air and 50% nitrogen except that the roast temperature was maintained at 640°C. The roast product was quenched in air, then magnetically separated using a laboratory Carpco induced roll magnetic separator.

The results in Table 1 for an XRD analysis of the magnetic fraction from the 640°C roast (at a 80 wt% mass recovery) show that it contained less rutile than the product from the higher roast temperature of 700°C in Example 1. Also, the rutile that was present had a crystallite size of only half of that obtained at the higher temperature. The mass solubility of the 640°C roast magnetic fraction in 71% sulfuric acid was 89.5% suggesting that it is likely to be suitable as a feedstock for a sulfate-route pigment plant. However, the grade of the magnetic fraction was 0.145 wt% Cr_2O_3 , which is higher than might be acceptable in a feedstock to a sulfate-route pigment plant.

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EXAMPLE 3

Another sample of the ilmenite concentrate used in Example 1 was given a similar roast for 45 min at 640°C in a 30 mm internal diameter fluidised bed reactor using a mixture of 80 wt% ilmenite plus 20 wt% of crushed char except that a gas mixture of nitrogen, carbon dioxide and water to simulate complete combustion of natural gas was used. The roast product was quenched in air, then magnetically separated using a laboratory Carpco induced roll magnetic separator.

The results in Table 1 show that a similar recovery (78 wt%) and grade of magnetic fraction (0.09 wt% Cr_2O_3) was obtained as for the 700°C roast in Example 1. The XRD analysis of this 640°C product showed that the main difference from the 700°C roast product was that the crystallite size of the rutile phase was only about half of that obtained at the higher roast temperature (Table 1). In contrast to the 700°C roast product, the 640°C roast product gave an acceptable mass solubility of 91% in the 71% sulfuric acid leach.

An XRD phase analysis of the 9 wt% of leach residue showed that it contained 84 wt% of rutile. Thus it contained 7.5 wt% of insoluble rutile relative to the roast product. As the roast product was analysed to contain 16% rutile, this means that over 50% of the rutile present in the roast product was leached in the 71% H_2SO_4 . A considerably higher proportion of the rutile would be expected to be leached in the stronger acid (~92% H_2SO_4) used in the sulfate-route process to titania pigment.

This example shows that the roast at 640°C gave a product, not only with a low chromia content, but also with a solubility in sulfuric acid that would be acceptable as a feedstock to sulfate pigment process as a result of the smaller grain size of the rutile, compared with that formed at 700°C, in the product.

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Table 1. Elemental and phase analyses (wt%) of head ilmenite sample and roasted magnetic fractions, together with rutile crystallite sizes and solubilities in H₂SO₄.

		Example 1	Example 2	Example 3
	Head ilmenite	Magnetic fraction from 700°C roast in air/N ₂	Magnetic fraction from 640°C roast in air/N ₂	Magnetic fraction from 640°C roast in N ₂ /CO ₂ /H ₂ O
Mass recovery (wt%)		81	80	78
<u>XRF analyses</u>				
TiO ₂		52.0		53.7
Fe ₂ O ₃		45.9	51.5	45.3
Cr ₂ O ₃		0.08	46.9	0.09
MnO		1.76	0.15	1.72
MgO		1.08	1.80	0.88
Al ₂ O ₃		0.40	1.10	0.37
SiO ₂		0.56	0.40	0.44
			0.45	
<u>Phase analyses</u> (from XRD)		69% ferrian ilmenite 13% pseudorutile 18% rutile	71% ferrian ilmenite 19% pseudorutile 10% rutile	69% ferrian ilmenite 21% pseudorutile 10% rutile
<u>Rutile crystallite size</u> (Å)		190	90	80
<u>Solubility</u> in 71% H ₂ SO ₄		79.3	89.5	91.0

EXAMPLE 4

Another sample of the ilmenite concentrate used in Example 1 was roasted for 30 min at 635°C in a 150 mm internal diameter fluidised bed reactor using a mixture of 80 wt% ilmenite plus 20 wt% of crushed char in gas mixture of nitrogen, carbon dioxide and water to simulate complete combustion of natural gas. The roast product was quenched in air, then magnetically separated using a laboratory Carpcu induced roll magnetic separator.

Table 2 shows that at a mass recovery of 83.5 wt%, the magnetic fraction contained 11 wt% rutile with a chromia assay of 0.11 wt% Cr₂O₃.

The 635°C roast product was digested with 92% H₂SO₄ under the conditions established by Grey, Lanyon and Stranger (1996) to give similar results in the laboratory to those obtained in a sulfate pigment plant. Digestion of the roast product gave a titania solubility of 93.9% TiO₂ and a soluble chromia content of 0.065% Cr₂O₃, both values indicating the product would be a suitable feedstock for a sulfate-route pigment plant.

Table 2. Elemental analyses (wt%) of head ilmenite concentrate sample and roasted magnetic fraction and digestion results in 92% H₂SO₄.

	Head ilmenite concentrate	Magnetic fraction from 635°C roast
Mass recovery (wt%)		83.5
<u>XRF analyses (wt%)</u>		
TiO ₂	52.5	53.3
Fe ₂ O ₃	44.5	45.7
Cr ₂ O ₃	0.70	0.11
MnO	1.77	1.75
MgO	0.94	0.95
Al ₂ O ₃	0.49	0.38
SiO ₂	0.48	0.47
<u>Digestion in 92% H₂SO₄</u>		
mass solubility (wt%)		93.6
TiO ₂ solubility (wt%)		93.9
Fe ₂ O ₃ solubility (wt%)		97.6
Cr ₂ O ₃ solubility (wt%)		55.8
Soluble Cr ₂ O ₃ (wt%)		0.065

EXAMPLE 5

A sample of another ilmenite concentrate containing 0.85 wt% Cr_2O_3 was roasted for 30 min at 575-585°C in a 150 mm internal diameter fluidised bed reactor using a mixture of 90 wt% ilmenite plus 10 wt% of crushed char in gas mixture of nitrogen, carbon dioxide and water to simulate complete combustion of natural gas. The roast product was quenched in air, then magnetically separated using a laboratory Carpcu induced roll magnetic separator. At a mass recovery of 80 wt%, the magnetic fraction contained 9.8 wt% rutile and 0.08 wt% Cr_2O_3 . When the 580°C roast product was digested with 92% H_2SO_4 it gave a titania solubility of 93.3% TiO_2 and a soluble chromia content of 0.043% Cr_2O_3 , both values indicating the product would be a suitable feedstock for a sulfate-route pigment plant.

Table 3. Elemental analyses (wt%) of head ilmenite concentrate sample and roasted magnetic fraction and digestion results in 92% H_2SO_4 .

	Head ilmenite concentrate	Magnetic fraction from 580°C roast
Mass recovery (wt%)		80
<u>XRF analyses (wt%)</u>		
TiO_2	52.5	54.1
Fe_2O_3	42.4	43.8
Cr_2O_3	0.85	0.08
MnO	2.00	2.08
MgO	0.82	0.78
Al_2O_3	0.70	0.41
SiO_2	0.77	0.60
<u>Digestion in 92% H_2SO_4</u>		
mass solubility (wt%)		94.5
TiO_2 solubility (wt%)		93.3
Fe_2O_3 solubility (wt%)		97.5
Cr_2O_3 solubility (wt%)		57.2
Soluble Cr_2O_3 (wt%)		0.043

EXAMPLE 6

Samples of another ilmenite concentrate containing 1.10 wt% Cr_2O_3 were roasted in a 30 mm internal diameter fluidised bed reactor at temperatures of 640, 600 and 550°C for times of 10, 30 and 60 minutes, respectively. A mixture of 80 wt% ilmenite plus 20 wt% of crushed char was used and the fluidising gas was a mixture of nitrogen, carbon dioxide and water to simulate complete combustion of natural gas. The roast product was quenched in air, then magnetically separated using a laboratory Carpco induced roll magnetic separator.

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For similar mass recoveries of 77-84 wt% as given in Table 4, the chromia contents of the magnetic fractions were similar at 0.10-0.12 wt% Cr_2O_3 showing that satisfactory chromia rejection can be achieved at temperatures between 640 and 550°C.

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Table 4. Elemental analyses (wt%) of head ilmenite concentrate sample and roasted magnetic fractions for roasts at different temperatures and times.

	Head ilmenite concentrate	Product from 640°C roast for 10 minutes	Product from 600°C roast for 30 minutes	Product from 550°C roast for 60 minutes
Mass recovery (wt%)		77	84	82
<u>XRF analyses</u>				
(wt%)	53.0	53.9	54.0	53.6
TiO_2	43.5	44.5	44.2	44.4
Fe_2O_3	1.10	0.12	0.095	0.115
Cr_2O_3	1.84	1.86	1.88	1.88
MnO	0.91	0.78	0.78	0.85
MgO	0.64	0.38	0.39	0.37
Al_2O_3	0.66	0.58	0.61	0.58
SiO_2				

EXAMPLE 7

- Samples of the ilmenite concentrate used in Example 5 were roasted in a 30 mm internal diameter fluidised bed reactor at a temperature of 575°C for 60 minutes. A mixture of 90 wt% ilmenite plus 10 wt% of crushed char was roasted
- 5 with a gas mixture of nitrogen, carbon dioxide and water to simulate complete combustion of natural gas with and without oxygen added to the gas mixture. The roast products were quenched in air, then magnetically separated using a laboratory Carpco induced roll magnetic separator.
- 10 For similar mass recoveries of 77.5-80 wt% as given in Table 5, the chromia contents of the magnetic fractions were similar at 0.08-0.11 wt% Cr_2O_3 indicating that a satisfactory chromia rejection can be achieved with a range of gas compositions. Also appreciable removal of alumina and silica has been achieved. Other results (eg Example 5) have shown that rutile present in these
- 15 products will be soluble in a 92% H_2SO_4 digestion.

Table 5. Elemental analyses (wt%) of head ilmenite concentrate sample and roasted magnetic fractions for roasts with char in different gas compositions.

	Head ilmenite concentrate	Product from 575°C roast. Gas = S*	Product from 575°C roast. Gas = S + 1% O_2
Mass recovery (wt%)		80	77.5
XRF analyses (wt%)			
TiO_2	51.4	54.0	53.3
Fe_2O_3	43.5	43.9	44.7
Cr_2O_3	0.84	0.08	0.11
MnO	1.93	2.10	2.09
MgO	0.91	0.77	0.81
Al_2O_3	0.68	0.38	0.38
SiO_2	0.84	0.60	0.58

- * S = gas mixture of nitrogen, carbon dioxide and water to simulate complete
- 20 combustion of natural gas.

EXAMPLE 8

Samples of another ilmenite concentrate containing 0.74 wt% Cr_2O_3 were roasted in a 30 mm internal diameter fluidised bed reactor at a temperatures of 640 and 575°C for 30 minutes. The samples were roasted in a gas mixture of
5 nitrogen, carbon dioxide and water to simulate complete combustion of natural gas. The roast products were quenched in air, then magnetically separated using a laboratory Carpco induced roll magnetic separator.

For the magnetic fraction at mass recoveries of 79 wt%, the chromia contents of
10 the magnetic fractions were similar at 0.08 and 0.10 wt% Cr_2O_3 indicating that a satisfactory chromia rejection was achieved with the gas composition. Also appreciable removal of alumina and silica has been achieved.

The results in Table 6 for the XRD analysis show that the magnetic fractions
15 from the 640°C roast contained 10 wt% rutile, with a crystallite size of 90 Å. The mass solubility of the magnetic fraction in 71% sulfuric acid was 92%. All these values indicate that this product will be a suitable feedstock for the sulfate process to titania pigment.

20 The results in Table 6 for the magnetic fraction from the 575°C roast show that it would be even more suitable as a feedstock for the sulfate process to titania pigment, as confirmed by its mass solubility in the 71% sulfuric acid leach of 93.6%.

Table 6. Elemental and phase analyses (wt%) of head ilmenite sample and roasted magnetic fractions, together with rutile crystallite sizes and solubilities in H_2SO_4 .

	Head ilmenite	Magnetic fraction from 640°C roast in $\text{N}_2/\text{CO}_2/\text{H}_2\text{O}$	Magnetic fraction from 575°C roast in $\text{N}_2/\text{CO}_2/\text{H}_2\text{O}$
Mass recovery (wt%)		79	79
<u>XRF analyses</u>			
TiO_2	53.1	54.0	53.9
Fe_2O_3	42.8	44.1	44.0
Cr_2O_3	0.74	0.08	0.10
MnO	1.90	1.96	1.96
MgO	0.84	0.85	0.85
Al_2O_3	0.58	0.32	0.33
SiO_2	0.76	0.53	0.53
<u>Phase analyses</u> (from XRD)		66% ferrian ilmenite 24% pseudorutile 10% rutile	59% ferrian ilmenite 34% pseudorutile 70% rutile
<u>Rutile crystallite size (Å)</u>		90	60
<u>Solubility</u> in 71% H_2SO_4		92.0	93.6

EXAMPLE 9

Samples of the ilmenite concentrate used in Example 8 were roasted in a 30 mm internal diameter fluidised bed reactor at temperatures between 640 and 525°C for 30 minutes. The samples were roasted in a gas mixture of nitrogen, carbon dioxide and water to simulate complete combustion of natural gas. The roast products were quenched in air, then magnetically separated using a laboratory Carpco induced roll magnetic separator.

For the magnetic fraction at mass recoveries of 79-81 wt% as shown in Table 7, the chromia contents of the magnetic fractions were 0.08 wt% Cr₂O₃ for the 640°C roast, increasing to 0.11 wt% Cr₂O₃ for the 550°C roast, indicating that a satisfactory chromia rejection can be achieved at these temperatures. Even at 525°C, a magnetic fraction containing 0.13 wt% Cr₂O₃ was obtained, indicating that good chromia rejection was achieved at this temperature also. Appreciable removal of alumina and silica was achieved at all temperatures.

Table 7. Elemental analyses (wt%) of head ilmenite sample and roasted magnetic fractions from roasts in nitrogen, carbon dioxide and water.

	Head ilmenite	Magnetic fraction from 640°C roast	Magnetic fraction from 600°C roast	Magnetic fraction from 550°C roast	Magnetic fraction from 525°C roast
Mass recovery (wt%)		79	80	81	80
<u>XRF analyses</u>					
	53.1	54.0	54.1	53.9	53.7
TiO ₂	42.8	44.1	44.3	44.3	44.4
Fe ₂ O ₃	0.74	0.08	0.10	0.11	0.13
Cr ₂ O ₃	1.90	1.96	1.97	1.95	1.95
MnO	0.84	0.85	0.85	0.85	0.87
MgO	0.58	0.32	0.33	0.34	0.35
Al ₂ O ₃	0.76	0.53	0.51	0.53	0.52
SiO ₂					

EXAMPLE 10

A sample of the ilmenite concentrate used in Example 5 was roasted in a 30 mm internal diameter fluidised bed reactor at a temperatures of 575°C for 30 minutes. The sample was roasted in a gas mixture of nitrogen, carbon dioxide and water to simulate complete combustion of natural gas. The roast product was quenched in air, then magnetically separated using a laboratory Carpcu induced roll magnetic separator.

For the magnetic fraction at a mass recovery of 80wt%, the chromia content of the magnetic fraction was 0.10 wt% Cr₂O₃ indicating that a satisfactory chromia rejection was achieved. Other results (eg Example 8) have shown that rutile in these products will be soluble in a 71% H₂SO₄ digestion and so the product would be a suitable feedstock for the sulfate route to titania pigment.

Table 8. Elemental analyses (wt%) of head ilmenite concentrate sample and roasted magnetic fractions for roasts in different gas compositions.

	Head ilmenite concentrate	Product from 575°C roast Gas = S*	
Mass recovery (wt%)		80	
<u>XRF analyses (wt%)</u>			
TiO ₂	51.4	54.0	
Fe ₂ O ₃	43.5	44.4	
Cr ₂ O ₃	0.84	0.10	
MnO	1.93	2.10	
MgO	0.91	0.81	
Al ₂ O ₃	0.68	0.39	
SiO ₂	0.84	0.62	

* S = gas mixture of nitrogen, carbon dioxide and water to simulate complete combustion of natural gas.

EXAMPLE 11

A sample of another ilmenite concentrate containing 0.29 wt% Cr_2O_3 was roasted in a dish in a tube furnace in a stream of nitrogen at a temperature of 600°C for 15 minutes. The roasted sample was cooled under nitrogen and then

5 magnetically separated using a laboratory Carpco induced roll magnetic separator.

A magnetic fraction was obtained at 85 wt% mass recovery with a chromia content of 0.06 wt% Cr_2O_3 .

10

The result in Table 9 shows that heating in nitrogen to order the structure in the mineral can give a magnetic enhancement of the titanium-containing mineral to allow a satisfactory rejection of chromia to be achieved.

15 Table 9. Elemental analyses (wt%) of head ilmenite concentrate sample and roasted magnetic fraction for a roast at 600°C in nitrogen.

	Head ilmenite concentrate	Magnetic fraction from 600°C roast
Mass recovery (wt%)		85.3
<u>XRF analyses (wt%)</u>		
TiO ₂	53.0	53.2
Fe ₂ O ₃	44.6	45.4
Cr ₂ O ₃	0.29	0.06
MnO	1.95	1.95
MgO	0.87	0.95
Al ₂ O ₃	0.35	0.28
SiO ₂	0.33	0.32

EXAMPLE 12

Samples of the ilmenite concentrate used in Example 8 were roasted in a 30 mm internal diameter fluidised bed reactor at a temperatures between 640 and 525°C for 30 minutes. The samples were roasted in nitrogen gas. The roast products were quenched in air, then magnetically separated using a laboratory Carpco induced roll magnetic separator.

For the magnetic fraction at mass recoveries of 79-82 wt%, the chromia contents of the magnetic fractions were 0.09 wt% Cr₂O₃ for the 640°C roast and 0.10 wt% Cr₂O₃ for the 550°C roast, indicating that a satisfactory chromia rejection was achieved at these temperatures. Even at 525°C, a magnetic fraction containing 0.13 wt% Cr₂O₃ was obtained, indicating that good chromia rejection was achieved at this temperature also. Appreciable removal of alumina and silica was achieved at all temperatures.

Table 10. Elemental analyses (wt%) of head ilmenite sample and roasted magnetic fractions from roasts in nitrogen.

	Head ilmenite	Magnetic fraction from 640°C roast	Magnetic fraction from 600°C roast	Magnetic fraction from 550°C roast	Magnetic fraction from 525°C roast
Mass recovery (wt%)		79	82	80	81
<u>XRF analyses</u>					
	53.1	54.0	54.0	54.0	53.4
TiO ₂	42.8	44.2	44.2	44.3	44.1
Fe ₂ O ₃	0.74	0.09	0.10	0.10	0.13
Cr ₂ O ₃	1.90	1.97	1.97	1.93	1.90
MnO	0.84	0.84	0.84	0.86	0.88
MgO	0.58	0.33	0.33	0.34	0.35
Al ₂ O ₃	0.76	0.52	0.52	0.52	0.53
SiO ₂					

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Walpole, E A, 1992. Improved process for separating ilmenite, (Austpac Gold NL) Au 9176298, 5 March 1992, Appl Au 902031, 30 August 1990, 22 pp.

Claims

1. A process for upgrading a primary ilmenite concentrate containing gangue mineral grains for production of titania pigment by the sulfate method,
5 the process comprising:
roasting a primary ilmenite concentrate containing gangue mineral grains at a temperature of less than 650°C in a gas atmosphere that aids the formation of a magnetically separable material rich in ilmenite and containing rutile at least partially soluble in concentrated sulfuric acid;
10 subjecting the roasted ilmenite concentrate containing gangue to magnetic separation to remove gangue mineral grains and provide a product rich in ilmenite and containing rutile.
2. A process according to claim 1 wherein the step of roasting the ilmenite
15 concentrate is carried out at a temperature such as to control the amount of rutile, and its crystalline size, formed so that a high proportion of the rutile is soluble in a sulfuric acid digestion as used in the production of titania pigment.
3. A process according to claim 1 wherein the step of roasting the ilmenite
20 containing gangue mineral grains is conducted at a temperature in the range of from 500 to 650°C.
4. A process according to claim 3 wherein the temperature is in the range of from 525 to 650°C.
25
5. A process according to claim 3 wherein the temperature is in the range of from 575 to 640°C.
6. A process according to claim 1 wherein the step of roasting the primary
30 ilmenite concentrate containing gangue mineral grains is carried out in an inert atmosphere, a non-reducing atmosphere or under an oxidizing atmosphere.

7. A process according to claim 1 wherein the step of roasting the primary ilmenite concentrate containing gangue mineral grains is carried out in a non-reducing gas atmosphere.
- 5 8. A process according to claim 1 wherein the step of roasting the primary ilmenite concentrate containing gangue mineral grains is carried out in an inert gas atmosphere.
9. A process according to claim 7 wherein the non-reducing gas
10 atmosphere comprises a mixture of carbon dioxide, nitrogen and water corresponding to fully combusted natural gas.
10. A process according to claim 8 wherein the inert gas atmosphere is nitrogen.
- 15 11. A process according to claim 1 wherein the oxygen partial pressure during the roasting step is controlled by using an excess of solid carbonaceous material.
- 20 12. A process according to claim 1 wherein the step of roasting is conducted in an oxidizing atmosphere.
13. A process according to claim 1 wherein the roasting is carried out for a period in the range of from 10 minutes to 4 hours.
- 25 14. A process according to claim 1 wherein the roasting is carried out for a period of from 15 to 60 minutes.
15. A process according to claim 1 wherein said product rich in ilmenite and
30 containing rutile is digested in sulfuric acid wherein at least part of the rutile is dissolved.
16. A process according to claim 1 where the roasting is carried out in an reactor selected from a fluidised bed that aids in the formation of a magnetically

separable material, a static bed and a rotary kiln furnace and wherein when the reactor is a fluidised bed the fluidising gas comprises said gas which aids in the formation of a magnetically separable material.

- 5 17. A process according to claim 1 in which the magnetic separation is achieved by using a magnetic separator selected from rare earth roll or drum magnetic separators wet high intensity magnetic separators, lift type magnetic separators and rotating magnetic field separators.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTERInt. Cl. ⁷: B03C 1/015, C01G 23/047, C09D 1/36.

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B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int. Cl. ⁷: B03C 1/015, C01G 23/047, C09D 1/36.

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

AU: C01G 23/- 1917-1947;.

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Derwent Online Abstracts, (B03C 1/015 or C01G 23/- or C09D 1/36 or C22B 1/02 or C22B 34/12) with keyword ilmenite, USPTO site full text search with keywords ilmenite\$, roast\$ and magnet\$, all period 1975-2002; ESP@CENET titles and abstracts, keyword "ilmenite," period 1920-1974.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5085837 A (CHAO et. al.) 4 February 1992. See column 4 lines 5-29..	1
X	Derwent Abstracts Accession No. 93-321060/40, Class P41 ZA 9204151 A (QIT-FER & TITANE INC.) 28 July 1993. See examples.	1-17
X	WO 94/12675 A (E.I. DU PONT DE NEMOURS AND CO.) 9 June 1994. See claims.	1
X	US 5490976 A (RENNIE et. al.) 13 February 1996. See col. 7 line 49 - col. 8 line 12.	1-17
A	US 5595347 A (WALPOLE) 21 January 1997. See examples.	1-17
A	US 4384883 A (FENSOM) 24 May 1983. See examples.	1-17



Further documents are listed in the continuation of Box C



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INTERNATIONAL SEARCH REPORT

International application No.

Information on patent family members

PCT/AU02/00538

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report				Patent Family Member			
US	5085837	US	4899015	AU	46837/89	EP	432321
ZA	9204151	NONE					
WO	9412675	AU	56109/94	CA	2149675	NO	952080
		NZ	258438	US	5378438	ZA	9308946
US	5490976	AU	42527/93	BR	9306615	EP	642595
		NO	944547	WO	9324669		
US	5595347	AU	76298/91	BR	9106829	CA	2090482
		CN	1060500	FI	930848	NO	930690
		NZ	239532	WO	9204121	ZA	9106845
US	4384883	AU	74553/81	EP	57706	NZ	198095
		WO	8200663	ZA	8105741		
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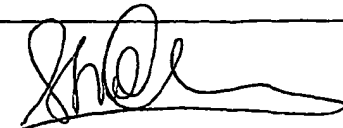
For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: **UPGRADING ILMENITE FOR TITANIA PRODUCTION**

(57) Abstract: The present invention provides a process for upgrading a primary ilmenite containing gangue mineral grains for forming titania pigment by the sulfate method, the process including the step of: roasting a primary ilmenite containing gangue mineral grains at a temperature of less than 650 °C under conditions that promote the formation of a magnetically separable product rich in titania and in which the rutile present is in a form that is at least partially soluble in concentrated sulfuric acid. The process will typically involve the step of: subjecting the roasted ilmenite concentrate containing gangue to magnetic separation to reduce the content of gangue mineral grains and provide a product rich in ilmenite and containing rutile.

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**REVISED
VERSION****INTERNATIONAL SEARCH REPORT**International application No.
PCT/AU02/00538

A. CLASSIFICATION OF SUBJECT MATTER												
Int. Cl. ⁷ : B03C 1/015, C01G 23/047, C09C 1/36.												
According to International Patent Classification (IPC) or to both national classification and IPC												
B. FIELDS SEARCHED												
Minimum documentation searched (classification system followed by classification symbols)												
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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched												
AU: C01G 23/- 1917-1947;.												
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)												
Derwent Online Abstracts, (B03C 1/015 or C01G 23/- or C09C 1/36 or C22B 1/02 or C22B 34/12) with keyword ilmenite, USPTO site full text search with keywords ilmenite\$, roast\$ and magnet\$, all period 1975-2002; ESP@CENET titles and abstracts, keyword "ilmenite," period 1920-1974.												
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Date of the actual completion of the international search 18 June 2002		Date of mailing of the international search report 3 JUL 2002										
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaaustralia.gov.au Facsimile No. (02) 6285 3929		Authorized officer  G. J. BROXAM Telephone No : (02) 6283 2133										

INTERNATIONAL SEARCH REPORT

Information on patent family members

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		NZ	258438	US	5378438	ZA	9308946
US	5490976	AU	42527/93	BR	9306615	EP	642595
		NO	944547	WO	9324669		
US	5595347	AU	76298/91	BR	9106829	CA	2090482
		CN	1060500	FI	930848	NO	930690
		NZ	239532	WO	9204121	ZA	9106845
US	4384883	AU	74553/81	EP	57706	NZ	198095
		WO	8200663	ZA	8105741		
END OF ANNEX							